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VI.—ON THE MEASUREMENT OF THE ELECTRICAL RESISTANCE OF POROUS MATERIALS.

By A. E. KNOWLER, *M.Sc., A.Inst.P.*, of the Building Research Station.

Received June 17, 1927.

(*Communicated by* A. F. DUFTON.)

ABSTRACT.

A method is described whereby the resistance of a material is measured independently of that at the surfaces in contact with it. The method is specially suited to the measurement of the resistance of ceramic, refractory, and building materials. Results show that the conductivity of a building stone is nearly proportional to its moisture content.

MANY measurements have been made of the resistance of ceramic, refractory and building materials. The published values, however, show great discrepancies, and for silica brick, for example, the figures of one authority are thirty times those of another.[1]

These discrepancies appear to be due mainly to lack of appreciation of the resistance at the ends of a specimen when it is inserted in an electrical circuit. Attempts have been made to reduce this resistance to a minimum. At the best,

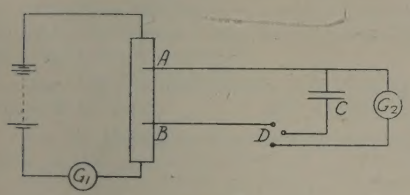


FIG. 1.

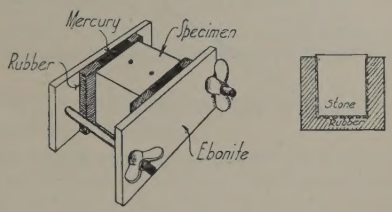


FIG. 2.

the resistance has been found by the author to be high and variable; a plaster-mercury contact was found to be as much as 50,000 ohms for 1 sq. cm.

The potentiometer method, whereby the resistance of a good conductor is measured independently of the resistances at its ends, is not sufficiently sensitive for materials of high resistivity. The method now described has been devised for the measurement of the resistance of building materials.

A measured current is passed through the specimen in which are inserted two wires, *A* and *B*, which assume the potential of the material at points a measurable distance apart (Fig. 1). The potential difference between the points is measured by charging the condenser *C* and discharging it through the ballistic galvanometer G_2. With materials of high resistance the condenser takes a long time to become

charged, so it is preferable to measure the potential difference with a quadrant electrometer.

Direct current can be used for dry materials; but when experiments were made with moist materials complications arose, which were traced to electroendosmosis (moisture movement caused by the current) and to electromotive force due to polarisation. These difficulties were avoided by the use of alternating current. This was taken from the mains at 200 volts, 50 cycles. It was found convenient to compare the potential drop in the material with that across a known resistance, the measurements being made with quadrant electrometers used idiostatically.

There is a possible source of error in the use of an electrometer for measurement of the A.C. potential. The quadrants, though small, have some capacity, and this has to charge up through the resistance between the material and the wires embedded in it. Increase in this resistance decreases the deflection. It was found,

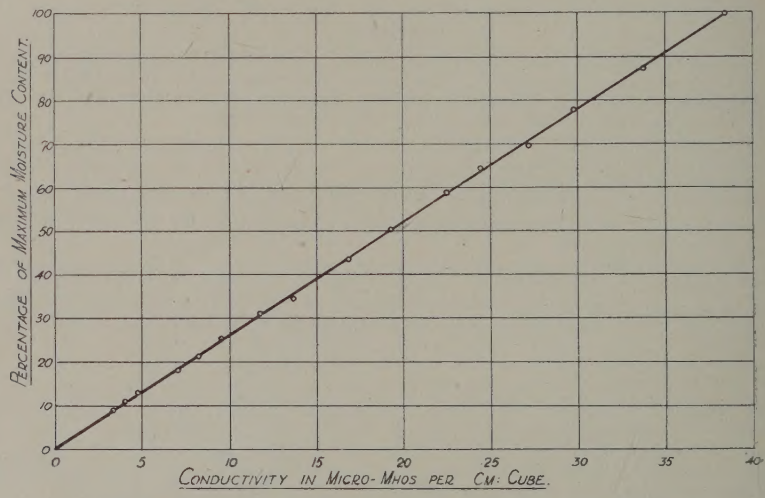


Fig. 3.—Corsham Stone Conductivity Concentration Curve.

however, that the error involved was negligible, being only 0·5 per cent. when the contact resistance was as large as 1 megohm.

The variation of the conductivity of a stone with its moisture content has been investigated. The specimens, which were $1'' \times 1'' \times 1\frac{1}{2}''$, were held in the clamp shown in Fig. 2, the wires *A* and *B* being inserted in holes $\frac{1}{2}''$ deep and 1/16″ diameter, which were filled with mercury. The moisture content was determined by weighing; the maximum moisture content is taken as that attained after the specimen has been soaking for three weeks. For the purposes of this Paper it is thought sufficient to show the results obtained with only one material, a limestone from Corsham Down. In Fig. 3 the conductivity of this stone is plotted against its moisture content. It will be seen that the curve is nearly a straight line and passes through the origin. The conductivity appears, therefore, to be almost entirely due to the moisture.

During the course of this work an interesting phenomenon was noticed. When the ends of a wet stone were connected to a galvanometer a current was observed which in some instances would change sign suddenly, but in others would remain approximately constant for week after week. It is suggested that this current is due to the non-uniform concentration of soluble salts in the stone. The electromotive force, which may be termed the "self-E.M.F." of the stone, is not large enough to affect the measurements; with a specimen of plaster the greatest value observed was only 0·05 volts.

References.

(1) Hartman, Sullivan, and Allen, J. Amer. Electrochem. Soc., 38, 279 (1920). Stansfield, MacLeod, and Mahon, J. Amer. Electrochem. Soc., 38, 574 (1920).

DISCUSSION.

Mr. J. H. Coste: The author states, "The conductivity appears, therefore, to be almost entirely due to the moisture." Having regard to the very small conductivity of water, the author will doubtless agree that the actual conductivity is due to the ions dissolved by the water taken up. If, as one presumes, distilled water was used, these ions must be derived mainly from the stone itself, and in the case of limestone would be Ca'' and CO_3'' or HCO_3', unless, of course, other more soluble salts were present.

The author does not state the actual water content of the stone from Corsham Down, but limestones may contain from about 1 to 12 per cent. of water, according to their physical character. The specific conductivity of an approximately saturated solution of calcium carbonate in distilled water containing 0·0016 per cent. $CaCO_3$ was about 30×10^{-6} mho. Having regard to the conductivities found by Mr. Knowler and the probable percentage of water, one appears bound to assume that other ions than those mentioned contribute to the conductivity.

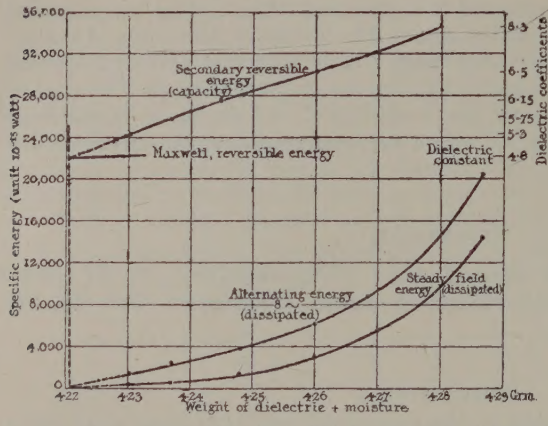
That the conductivity of stone and such materials is due to the effect of moisture seems a necessary conclusion, as no obvious means of producing detachable electrons except by ionic dissociation seems applicable.

The author's method may have some application in examining the hygroscopic state of stones in buildings.

Dr. B. A. Keen: Many investigations similar to those described in the Paper have been made on wet plastic materials, such as soil and clays, and also on soils that have been ignited to destroy their colloidal properties. In the latter material a linear relation obtains between conductivity and moisture content over the greater part of the moisture range; but when the moisture falls to 7 per cent. the curve bends sharply towards the conductivity axis. It is still linear, but cuts the moisture axis at 3·5 per cent. These results are quite reproducible. The interest of these discontinuities lies in the light they throw on the distribution of water in a granular mass. Calculations for an aggregation of spheres show that with cubical packing a continuous film of water over the spheres just ceases to be possible at a moisture content of 8 per cent., owing to the increasing curvature of the menisci in the annular wedge-shaped regions surrounding the points of contact. Similar calculations for close packing show a corresponding value of 3·5 per cent. The correspondence of these values with experimental determinations indicates the rupture of the film of water over the grains at 8 per cent., which allows a redistribution of the remaining water under surface tension. This process goes on until the last films break, and the remaining water is left in a series of isolated wedges throughout the mass. The author might try materials of a more granular structure—*e.g.*, oolitic limestone and sandstones—and see whether the theoretical results, confirmed for soil, also apply in these cases.

Mr. G. L. Addenbrooke sketched curves illustrating work described by him in *Nature*,

April 5, 1924, in which the moisture content of celluloid was plotted as abscissa against (1) a function of the capacity (upper curve); (2) the energy dissipated by A.C. at 8 cycles; and (3) the energy dissipated by D.C., the R.M.S. voltage being 100 in each case, the temperature 13 degrees, the area of the electrodes 125 cm.², and the thickness of dielectric 0·037 cm. The celluloid was dried at 100 degrees and the moisture admitted to it step by step. Extrapolation near the origin suggested that the resistance of perfectly dry celluloid would be infinite. The capacity is independent of the frequency in the dry material, but decreases with increasing frequency in moist material.



Dr. F. E. SMITH disagreed with the author's statement that the potentiometer method is less sensitive than that described in the Paper. He also thought that the potentiometer method is easier to carry out.

Dr. E. H. RAYNER asked Dr. Keen why he had chosen to make an artificial material by igniting soil. How did the resistance of natural clay compare with that obtained by his theory and experiments?

Dr. B. A. KEEN: In answer to Dr. Rayner, natural soils show very different types of curve from those shown by ignited soil. The measurements can in fact be used to throw light on the cause of this difference, which is associated with the presence of colloidal material in a kind of skin over the soil particles. This colloidal material is removed or rendered inert by ignition.

THE AUTHOR: (In reply to Mr. J. H. Coste): The Corsham stone used was saturated by 11 per cent. of its weight by water. It was hoped to use these resistance measurements to determine the distribution of water in building stones, but it was found the method was not practicable. (In reply to Dr. B. A. Keen): Measurements have been made with a sandstone, Robinhood; and a limestone, Monks Park. Though the curves pass through the origin, they do not consist of single straight lines, but of two straight lines at an angle, and meeting at about 3 per cent. of moisture (60 per cent. of total moisture content). It is supposed that the first 3 per cent. goes to fill the fine pores in the cementing material, the remainder going to fill the interstices between the grains. The kink in the curve corresponds to the "fibre saturation point" of wood. Even when the moisture content is very low there should be a continuous water film due to adsorption, and this should be conducting. (In reply to F. E. Smith): The potentiometer method has been used; but, whereas the sensitivity of the method here described is the same whatever the resistance, the sensitivity of the potentiometer decreases with increase in resistance. It can be used in these experiments only for stones that are nearly saturated. If a stone is nearly dry the contact can be shifted over a wide range, the galvanometer giving no deflection. The galvanometer gave one mm. deflection for two micro-amps. With a dry stone there is a huge contact resistance between the mercury and stone, and this greatly decreases the sensitivity.

VII.—REGULARITIES IN THE SPECTRUM OF IONISED NEON.

II.

By P. K. Kichlu, *M.Sc.*, Research Scholar, University of Allahabad.

Received August 17, 1927.

(*Communicated by* Prof. A. O. Rankine, D.Sc.)

Abstract.

In a previous Paper on the same subject, the author traced a system of quartet terms in the known spectrum of ionised neon. In the present Paper the theory of Hund is applied in tracing doublet terms and intercombinations between doublets and quartets. Almost all the lines between 2,500 and 3,800 have been accounted for, with a few discrepancies.

IN the first Paper,* communicated to this Journal some time ago, the spectrum of ionised neon was discussed from the standpoint of modern theories of spectra, and it was shown that, in the list of ionised neon lines given by L. and E. Bloch† and Dejardin, a system of quartet terms is strongly developed. This work has been continued, and considerably more evidence has been brought forward to show the existence of further regularities in the spectrum.

In order to get a general idea of the whole spectrum, it is perhaps best to write out the terms that we might expect to find in Ne^+ on the theory of Hund. The arrangement of electrons in an atom of ionised neon is very well represented according to the following scheme due to Prof. M. N. Saha :—

Structure Diagram of Ne^+ (9).

K_1	L_1	L_2			
2	2	5			
		M_1	M_2	M_3	
			N_1	N_2	

The calculated terms are given below :—

Position of valence electrons.	Terms (calculated).	Terms (observed).
$5L_2$	a^2P	
↓		
$4L_2M_1$	$b^4\bar{P}$ b^2D b^2S $b^2\bar{P}$	$b^4\bar{P}$ $b^2\bar{P}$
↓		
$4L_2M_2$	$c^4\bar{D}$ c^4P $c^4\bar{S}$ $c^2\bar{D}$ c^2P $c^2\bar{S}$	$c^4\bar{D}$ c^4P $c^4\bar{S}$ $c^2\bar{D}$ c^2P $c^2\bar{S}$
↓		
$4L_2M_3$	$d^4\bar{F}$ d^4D $d^4\bar{P}$ $d^2\bar{F}$ d^2D $d^2\bar{P}$	$d^4\bar{F}$ d^4D $d^4\bar{P}$ d^2D $d^2\bar{P}$
$4L_2N_1$	$e^4\bar{P}$ e^2D e^2S $e^2\bar{P}$	

The quartet terms to be expected on this scheme have been derived in the first

* P. K. Kichlu, Proc. Phys. Soc. After this Paper was published, Mr. de Bruin, of Amsterdam, published a partial analysis of the Ne^+ spectrum in the Zs. f. Physik., Vol. 93.

† L. et E. Bloch et Dejardin, Jour. de Phys., Vol. 7, p. 129 (1926).

Paper. In this Paper we will discuss the doublet terms, and intercombinations between doublets and quartets.

The Doublet Spectrum.

Considerable difficulties were experienced in unravelling the doublet nature of the spectrum which is predicted on Hund's theory. No starting point like the multiplet utilised in the analysis of the quartet terms was available. The terms that have been obtained agree well with the theoretical considerations, though in certain cases discrepancies with regard to values and strengths have been noted.

As in the case of the quartet system, the deepest doublet terms so far observed originate from the configuration $4L_2M_1$. From this combination we expect $b^2\overline{P}$ and b^2D, b^2S, $b^2\overline{P}$, being the deepest, because it arises from ^3P of $4L_2$, while ^2D and ^2S arises from $^1\overline{D}_2$, $^1\overline{S}_0$, others decreasing in the regular order. But only $b^2\overline{P}$

The Multiplets.

——	$b^2\overline{P}_1$ 612·3	$b^2\overline{P}_2$
$c^2\overline{D}_2$ 511·0	26823·0 (9*R*)	27435·3 (5)
$c^2\overline{D}_2$ 1787·0		26924·2 (10*R*)
$c^2\overline{S}_1$ 1494·0	28098·8 (4)	28711·2 (6)
c^2P_1 127·0	29592·4 (5)	30204·8 (3)
c^2P_2	29465·7 (7)	30077·5 (7)

Multiplets between the Doublet Terms of the Combination $4L_2M_2$ and $4L_2M_3$.

	$c^2\overline{D}_2$ 511·0	$c^2\overline{D}_3$	$c^2\overline{S}_1$	c^2P_1 127·0	c^2P_2
d^2D_2 204·4	28951·6 (3)	[29462·5]*	27675·0 (4)	26181·5 (6)	26308·4 (4)
d^2D_3	28746·8 (3)	29257·3 (2)			26104·0 (7)
d^2P_1	22372·4 (3)			29601·9 (1)	
d^2P_2	31890·4 (2)	32311·4 (4)	30524·2 (2)	29029·8 (2)	29157·1 (5)
B			28922·6 (3)	27428·0 (3)	27554·4 (4)
C			28534·1 (5)	27040·0 (0)	27167·7 (2)

* This line falls very near the strong line 29465·7 (7) and is probably masked by it.

have been observed. It may be, under different conditions, b^2D and b^2S will also appear, but there is no possibility of their being represented so strongly. All the terms of the combination $4L_2M_2$, and some of the combination $4L_2M_3$, have been observed.

It will be seen that of the terms which we expect from the combination $4L_2M_3$ only d^2D have been identified with certainty. The reality of the term designated $^2P_2$ is unmistakable, but the want of a sure companion has made the identification rather obscure. The term here called $^2P_1$ explains only two lines, though more or less exactly. The natures of B and C have not been determined. B appears to be of the nature of $^2S_1$. No such place from the theoretical scheme can, however, be given to it. An S term is certainly to be expected from $4L_2M_3$, but this will probably be very weak, coming from remote combinations.

All the quartet and doublet terms so far observed are inverted—i.e., those with higher quantum numbers have also the higher value. The rule laid down by the Hund that of the terms arising from the same configuration those with the highest azimuthal quantum numbers are the deepest, is not being strictly obeyed. The order in many cases has been upset.

Intercombination Lines.

A reference to the author's first Paper will show that there are many levels, designated variously as α, β, γ . . . whose presence has been well established, but whose natures could not be exactly ascertained. As was suspected, some of the lines that these terms give rise to have turned out to be intercombination lines between doublet and quartet systems. The terms called α and β are actually d^2D_2 and d^2D_3 respectively, and combine with the quartet terms of the configuration $4L_2M_3$, and give the multiplets noted below :—

——	d^2D_3	204·4	d^2D_2
c^4P_1	33875·2 (1)		
c^4P_2	34058·2 (0)		33852·8 (0)
c^4P_3	34280·9 (1)		34076·6 (1)
c^4D_1	30634·1 (2)		
c^4D_2	30777·8 (3*dr*)		30573·7 (2)
c^4D_3	?		30822·8 (2)
c^4D_4			?
c^4S_2	27519·6 (1)		27315·3 (2)

The intercombination lines are occurring frequently. The $c^2\overline{D}-d^4\overline{F}$ multiplet given below is quite prominent.

——	$c^2\overline{D}_2$	511·0	$c^2\overline{D}_3$
$d^4\overline{F}_2$	29649·3 (3)		30160·7 (1)
$d^4\overline{F}_3$	29503·4 (5)		30014·2 (1)
$d^4\overline{F}_4$			29689·3 (6)
$d^4\overline{F}_5$			

All the lines explained by the doublet terms and intercombinations between doublets and quartets have been collected in Table I.

TABLE I.

λ	I	ν (vac.)	Combination	λ	I	ν (vac.)	Combination
2692·47	0	37129·7	$c^4P_3-d^2\overline{P}_2$	3443·75	2	29029·8	$c^2P_1-d^2\overline{P}_2$
2722·2	0	36724·2	$c^4P_1-d^2\overline{P}_2$	3453·05	3	28951·6	$c^2\overline{D}_2-d^2D_2$
2916·22	1	34280·9	$c^4P_3-d^2D_2$	3456·52	3	28922·6	$c^2\overline{S}_1-B$
2933·71	1	34076·6	$c^4P_3-d^2D_3$	3477·66	3	28746·8	$c^2\overline{D}_2-d^2D_3$
2935·29	0	34058·2	$c^4P_2-d^2D_2$	3481·97	6	28711·2	$b^2\overline{P}_2-c^2\overline{S}_1$
2951·15	1	33875·2	$c^4P_1-d^2D_2$	3503·58	5	28534·1	$c^2\overline{S}_1-C$
2953·10	0	33852·8	$c^4P_2-d^2D_3$	3522·7	0	28379·1	$c^4\overline{S}_2-C$
2973·03	1	33625·9	$c^4\overline{D}_2-d^2\overline{P}_2$	3537·98	3	28256·7	$b^2\overline{P}_1-c^4\overline{S}_2$
2986·0	0	33479·0	$c^4\overline{D}_1-d^2\overline{P}_2$	3546·06	1	28192·3	$c^2\overline{S}_1-\varepsilon$
3088·16	3	32372·4	$c^2\overline{D}_2-d^2\overline{P}_1$	3554·39	1	28126·2	$c^2\overline{D}_3-d^4D_1$
3093·99	4	32311·4	$c^2\overline{D}_3-d^2\overline{P}_2$	3557·86	4	28098·8	$c^2P_1-c^2S_1$
3135·79	1	31880·7	$b^4\overline{P}_3-c^2\overline{D}_3$	3574·23	0	27970·1	$c^2\overline{S}_1-\gamma$
3143·70	2	31800·4	$c^2\overline{D}_2-d^2\overline{P}_2$	3612·35	4	27675·0	$c^2\overline{S}_1-d^2D_2$
3160·0	0	31636·2	$c^4\overline{D}_2-C$	3628·09	4	27554·9	c^2P_1-B
3187·61	2	31362·4	$b^4\overline{P}_2-c^2\overline{D}_3$	3632·74	1	27519·6	$c^4\overline{S}_2-d^2D_2$
3243·42	2	30822·8	$c^4\overline{D}_3-d^2D_3$	3643·90	5	27435·3	$b^2\overline{P}_2-c^2\overline{D}_2$
3248·16	$3dr$	30777·8	$c^4\overline{D}_2-d^2D_2$	3644·87	3	27428·0	c^2P_1-B
3263·40	2	30634·1	$c_1\overline{D}_1-d^2D_2$	3659·91	2	27315·3	$c^4\overline{S}_2-d^2D_3$
3269·84	3	30573·7	$c^4\overline{D}_2-d^2D_3$	3679·79	2	27167·7	c^2P_2-C
3275·15	2	30524·2	$c^2\overline{S}_1-d^2\overline{P}_2$	3697·1	0	27040·0	c^2P_1-C
3309·78	3	30204·8	$b^2\overline{P}_2-c^2P_1$	3701·79	3	27006·3	$c^2P_2-d^4\overline{F}_2$
3314·62	1	30160·7	$c^2\overline{D}_3-d^4\overline{F}_2$	3713·07	$10R$	26924·2	$b^2\overline{P}_2-c^2\overline{D}_3$
3323·79	7	30077·5	$b^2P_2-c^2P_2$	3721·87	2	26860·6	$c^2P_2-d^4\overline{F}_3$
3330·80	1	30014·2	$c^2\overline{D}_3-d^4\overline{F}_3$	3727·09	$9R$	26823·0	$b^2\overline{P}_1-c^2\overline{D}_2$
3345·49	3	29882·4	$c^2\overline{S}_1-d^4\overline{P}_1$	3744·66	3	26697·1	$c^2P_1-\varepsilon$
3367·25	6	29689·3	$c^2\overline{D}_3-d^4\overline{F}_4$	3753·79	4	26632·2	$c^2P_2-\pi$
3371·80	3	29649·3	$c^2\overline{D}_3-d^4\overline{F}_2$	3799·99	4	26308·4	$c^2P_2-d^2D_2$
3377·19	1	29601·9	$c^2P_1-d^2\overline{P}_1$	3818·41	6	26181·5	$c^2P_1-d^2D_2$
3378·28	5	29592·4	$b^2\overline{P}_1-c^2P_1$	3829·75	7	26104·0	$c^2P_2-d^2D_3$
3388·47	5	29503·4	$c^2\overline{D}_2-d^4\overline{F}_3$	3942·19	3	25359·4	$b^2P_2-c^4D_3$
3392·81	7	29465·7	$b^2\overline{P}_1-c^2P_2$	3999·41	1	24996·6	$b^2P_1-c^4\overline{D}_2$
3414·83	1	29275·7	$c^2\overline{D}_2-\pi$	4522·65	4	22104·7	$b^2\overline{P}_2-c^4P_3$
3416·97	2	29257·3	$c^2\overline{D}_3-d^2D_3$	4565·3	0	21898·0	$b^2\overline{P}_1-c^4P_1$
3428·71	5	29157·1	$c^2P_2-d^2\overline{P}_2$				

Concluding Remarks.

The present analysis brings out all the essential details of the spectrum of Ne^+, and has been shown to fit in remarkably well with Hund's theory. The available data extend only from 2500 Å to 5000 Å, and almost all the lines in the ultra-violet part of the spectrum below 3800 Å, with few exceptions, have been explained. This part of the spectrum occurs as a distinct group of lines, lying removed from the rest. All attempts to classify lines in the higher wavelength region have proved unfruitful. The present analysis does not seem to afford any clue to their ordering, though it may be remarked that there are many pairs of lines with strong intensities, having intervals of c^4P, c^2P terms. Some of these are shown in the list of lines given in the first Paper. The lines with c^2P intervals are given below :—

c^2P_1	127	c^2P_2
22611·0 (4)		22483·7 (2)
22762·6 (7)		22634·6 (2)
22798·7 (2)		22672·9 (7)

Nothing can be said about their origin, and it is possible that these are purely chance coincidences.

As has already been remarked, the deepest terms so far found come from $4L_2M_1$ combination. The lines coming from the b^2P terms of the $5L_2$ combination obviously lie in the far Schumann region. It is hoped in the near future to examine this part of the spectrum experimentally with a vacuum spectrograph.

The work outlined in this Paper was carried out under the direction of Prof. M. N. Saha, F.R.S., and in concluding the Paper the author records his best thanks to Prof. Saha for his interest and encouragement during the progress of the research.

VIII.—A CALORIMETER FOR THE DETERMINATION OF THE HEAT DEVELOPED BY FRUIT.

By Ezer Griffiths, *D.Sc.*, *F.R.S.*, Physics Department, The National Physical Laboratory.

Received October 5, 1927.

Abstract.

A calorimeter for measuring the heat evolved by apples during the senescence stage is described. A differential arrangement is used, one container being filled with apples and the other with dummy apples of the same thermal capacity, made of thin-walled glass spheres filled with moistened glass wool. These containers are enclosed in a metal box thermally insulated, and set up in a constant temperature room. Resistance thermometers composed of 80 yards of nickel wire in glass tubes are disposed among the apples and the dummies. They are connected differentially to a slide wire, on which a difference of one thousandth of a degree causes a movement of the contact maker of 3 millimetres. The air circulation is controlled so as to maintain at will atmospheres containing from 2 to 10 per cent. of CO_2 around the apples. The moisture content of the air before and after circulation is determined by a dew-point apparatus, and a correction applied for the heat absorbed in evaporating water from the apples.

The results show that at a temperature of 20°C. sound apples generate heat at the rate of about 0·012 calorie per second per kilogram of apples. Or for an apple of average size (2½ inches in diameter) the rate of heat generation per second is one and a half thousandth calories.

IT has long been known that fruit generates heat by some process analogous to "respiration," but the quantitative determination of this heat evolution is a problem of considerable experimental difficulty.

A knowledge of the rate of heat production by apples in various stages of ripeness would be of value to both the plant physiologist and the refrigerating engineer. The theoretical interest of the problem is that quantitative data might help to elucidate the nature of the complex reactions taking place in apples which involve the oxidation of sugar and malic acid, and result in the evolution of carbon dioxide and other products in minute quantities.

The practical interest of the problem is that the refrigerating engineer has to contend with the heat generated by quantities of the order of 2,000 tons of apples stowed in the insulated holds of a ship.

Principle of Method Employed.

In devising a method for the measurement of the heat evolution by fruit, the conditions of the experiment must be so arranged that it is possible to maintain any desired composition of the atmosphere around the fruit. Hence provision has to be made for ventilation of a controlled amount. In the experiments to be described, atmospheres containing from 2 to 10 per cent. of carbon dioxide have been maintained at will over periods of several days at each concentration of carbon dioxide.

The method employed was a differential one. Two identical containers were made—one to contain apples, and the other "dummy" apples, consisting of thin walled glass spheres filled with glass wool soaked in water, to give the "dummy" approximately the same heat capacity as an apple of the same size.

Differential resistance thermometers were constructed in the form of two sets

of eight tubes projecting into the enclosures. Each of the tubes contained about 10 yards of nickel wire uniformly wound to occupy the full length of the tube. The object of this arrangement was to distribute the resistance thermometer coil over the space occupied by the apples and the dummies. All the coils in one enclosure were connected in series and constituted one thermometer, the corresponding coils in the other enclosure forming the other thermometer. These were connected to a slide wire bridge, on which one centimetre movement along the slide wire corresponded to a change of temperature of 0·003°C. between the thermometers.

The two enclosures were painted black, so as to ensure uniformity in the emissivities of their surfaces.* They were supported on wooden knife edges in a larger rectangular metal box well lagged on all sides with granulated cork. The large box was set up in the centre of a small room, whose temperature was maintained constant by a thermostat, heaters and a circulating fan. Rubber pipes were connected to the enclosure in which the apples were placed, so as to permit of the circulation at a steady rate of fresh air through the fruit.

Since the air which had been in contact with the apples was of a different humidity to the room air, and in the process of evaporation of moisture from the fruit heat is absorbed, arrangements were made to determine the humidities of the atmosphere in the large enclosure, and also of the stream of air drawn from the container in which the apples were situated.

The general arrangement of the apparatus is shown diagrammatically in Figs. 1 and 2, while Fig. 3 shows the thermostat arrangement for maintaining a constant temperature in the room in which the apparatus was situated.

The apparatus in the top left-hand corner, Fig. 1, is the aspirator for maintaining the circulation of air through the enclosure. By regulating the number of drops per second of the water from the constant head tank, a range of air speeds could be secured. The relation between the number of drops per second and the time for the passage of 1/1000 cu. ft. of gas through the apparatus is given in Table I below.

TABLE I.

Time in minutes for $\frac{1}{1000}$ cu. ft. of gas to circulate through apparatus.	Drops of water per minute.
0·5	284
1·0	129
1·5	86
2·0	66
2·5	56
3·0	49

The procedure in an experiment was as follows: The "zero" of the bridge was determined by packing both enclosures with "dummy" apples, and observing the bridge wire setting after the lapse of 24, 48 and 60 hours respectively. If these readings were in close agreement, it was presumed that the interior of the box was at a constant temperature, and that the two thermometers were in equilibrium. The bridge wire reading constituted the datum mark from which all subsequent

* In some of the preliminary experiments the space between the calorimeters and the container was packed with thin cork shavings; this reduced the thermal transfer to about half its value.

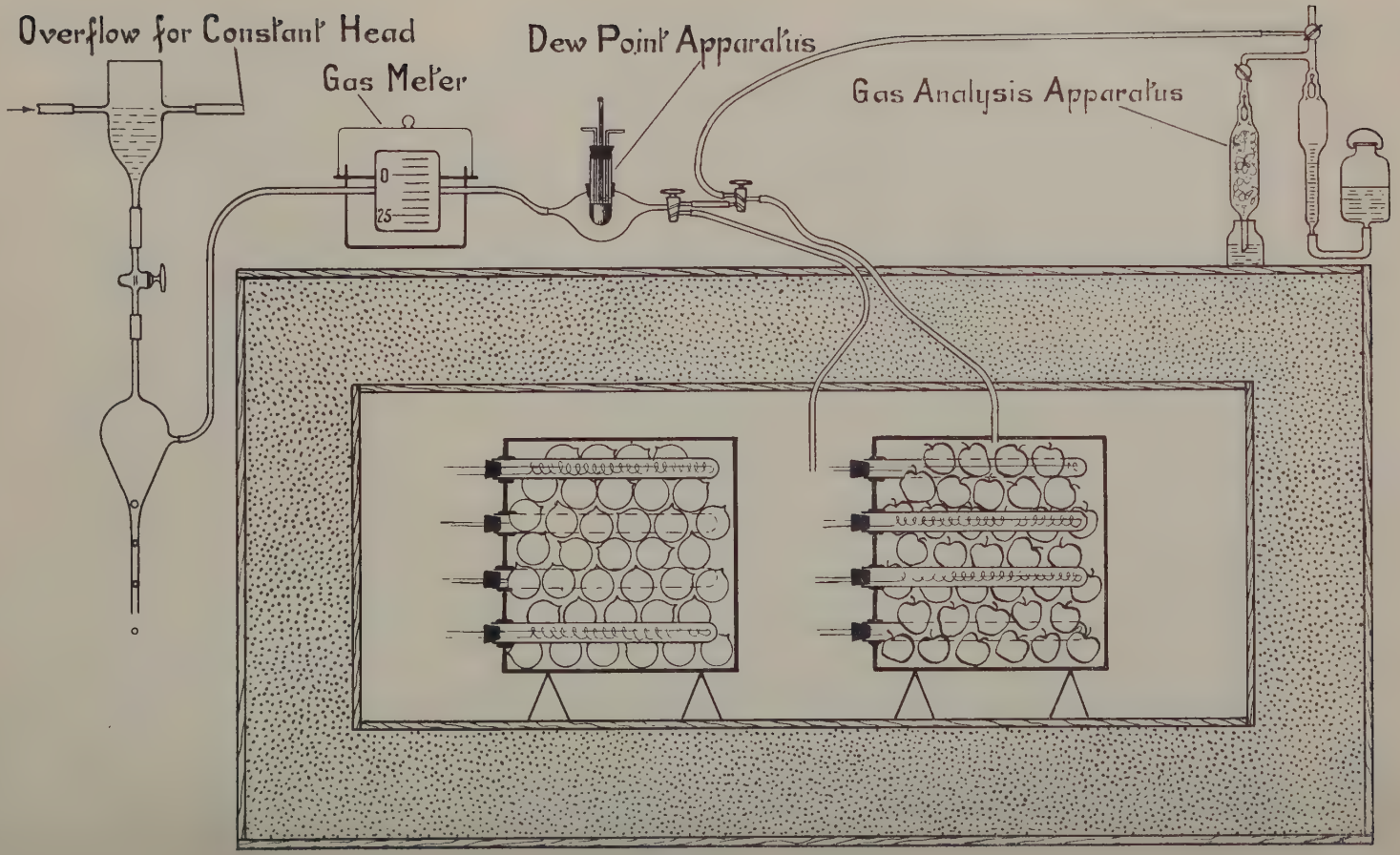

Overflow for Constant Head
Gas Meter
Dew Point Apparatus
Gas Analysis Apparatus
0
25

Fig. 1.

readings were measured. The " zero " was always checked at the completion of a series.

Having obtained the equilibrium point on the bridge wire, the " dummy " apples in the one enclosure were replaced by sound apples. The rate of gas flow through the apparatus was adjusted so as to give the desired percentage of carbon dioxide in the atmosphere around the apples. Usually percentage of carbon dioxide from 2 to 10 were employed. The apples generated heat, and consequently the bridge reading changed in the direction indicating that the thermometer in the enclosure containing apples was at a higher temperature than the one among the dummy apples. The order of magnitude of the temperature rise was 0·15°C. Periodically bridge wire readings, humidities of the atmosphere in the box and in the enclosure containing the apples were taken, and also an analysis made of the gas drawn off from the apparatus.

In order to convert the readings obtained on the bridge wire into rate of heat

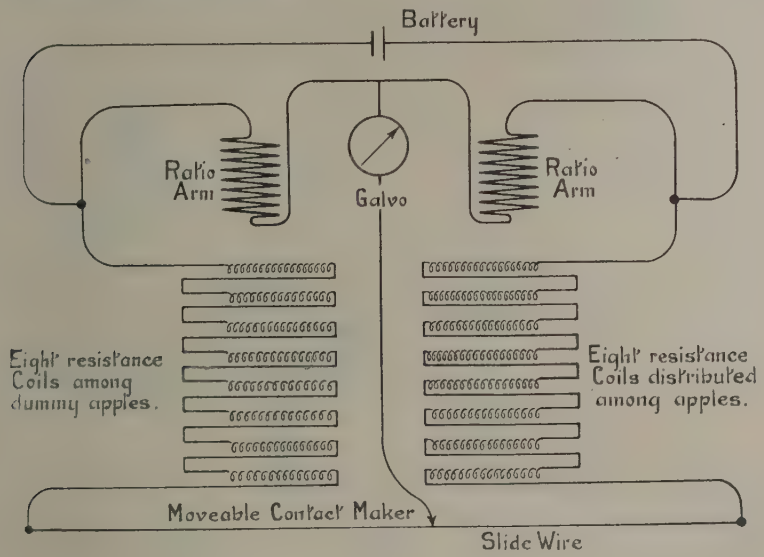


FIG. 2.

evolution by the apples in the container the apparatus was calibrated as follows: The apples were replaced by dummy apples, and a heating coil composed of 80 yards of cotton-covered copper wire was interspersed around the " dummy " apples. This coil was connected to a battery with a sensitive ammeter in series, a voltmeter was connected across its terminals so that the watts dissipated in the coil could be determined. For a steady rate of heat evolution the temperature rise was determined in a precisely similar manner to that adopted in an experiment with apples in the enclosure. The relation between energy generated in the coil and bridge reading was a linear one: a temperature rise of 0·1°C. or 0·02 ohms corresponding to an energy input of 0·037 calories per second.

In order to ascertain whether the distribution of the coil in the enclosure had

any influence on the reading, a check experiment was made, in which the heating coil was pressed up into a compact ball the size of an apple, and placed in the centre plane of the enclosure one layer up from the bottom. The rise in bridge reading

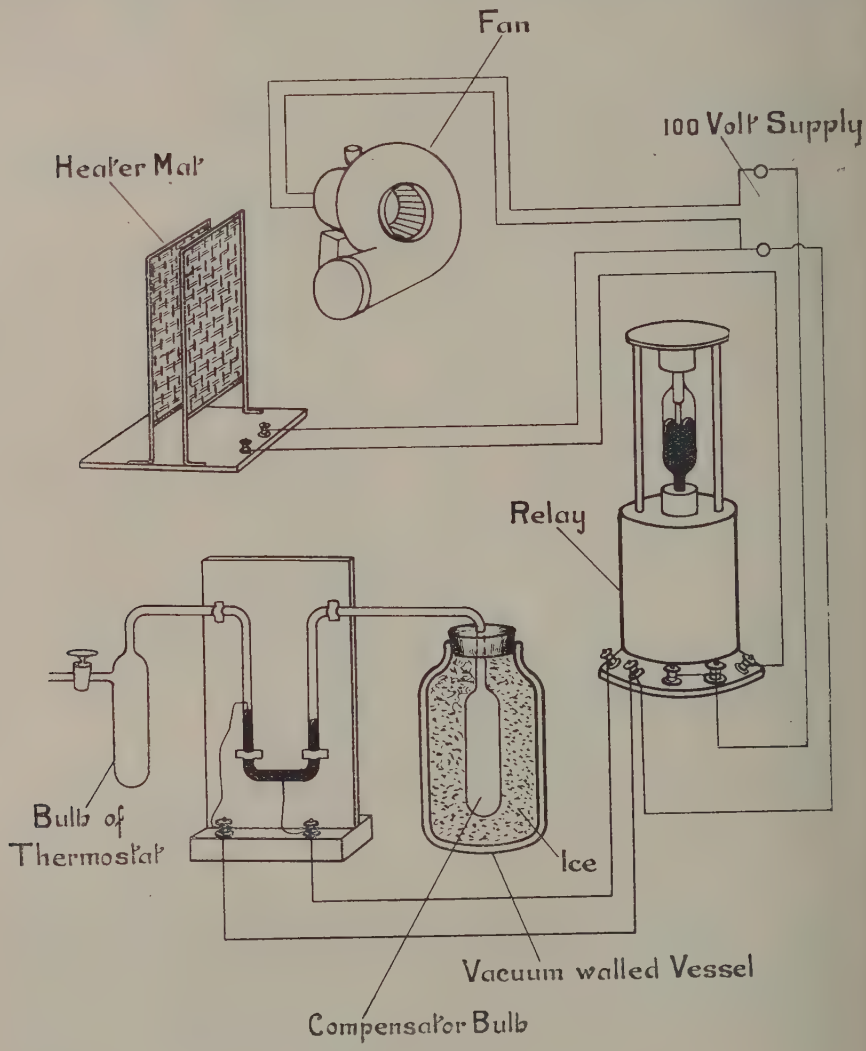


FIG. 3.

now produced by a given current through the coil differed from the observed when the coil was distributed by 4 per cent. This is an extreme test to apply to the apparatus, and it is unlikely that an uncertainty of anything like this magnitude

exists in the calibration results, since the distributed heating coil generated heat throughout the volume in a manner simulating the apples.

Another check experiment carried out was to ascertain whether the air circulation through the apparatus removed a measurable amount of heat due to the warming up of the air. This was, of course, for the case when no change in moisture content of the air was produced during its passage through the enclosure. That this effect was negligible was proved in two ways :—

(1) When a steady temperature in the enclosure had been obtained for a certain quantity of energy expended in the heating coil, the circulating pump was started and air drawn through at a slightly faster rate than the maximum employed in an actual experiment. No measurable effect on the bridge reading could be observed.

(2) Calculations were made assuming the volume of air circulated per minute, its temperature rise and the specific heat of air ; these calculations showed that the

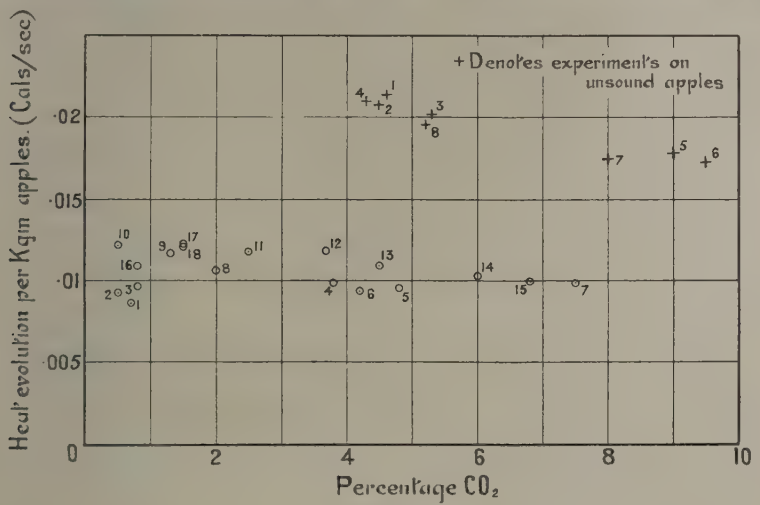


FIG. 4.

maximum amount of heat carried off by the air stream was only 0·3 per cent. of that normally generated by the apples.

The heat absorbed in evaporation of moisture from the apples was of a very different magnitude, and, in extreme cases of rapid circulation, amounted to 8 per cent. of the heat evolution of the apples.

Numerous series of experiments have been made, and a typical set is reproduced in Table II. The results of another two series on different batches of apples is shown in Fig. 4.

In one series, Fig. 4, the apples studied were unsound, most of them containing codling moth. The heat evolution for this consignment was considerably greater than in the case of the others tested.

In studying Fig. 4 it should be remembered that abscissæ give the percentage of carbon dioxide in the atmosphere around the apples, and not the rate at which carbon dioxide is generated.

TABLE II.

Bridge zero, 0·0470. Experiments at 20°C. Weight of apples = 11 lbs. 4½ ozs. = 5·12 kgm.

Date (time).	% CO_2.	Bridge	Pump Drops min.	Time for $\frac{1}{100}$ c. ft. by gas-meter.	Humidity of air from enclosure containing the apples. %	Humidity of air from large enclosure. %	Heat evolution from calibration		Heat abstracted by air current.		Total.	Cals./sec. per kgm.
							Bridge rise.	Cals./sec.	Hum. diff.	Cals./sec. taken from box.		
Jan. 31 (10.30)	2·2	0·0831	350	43 sec.	92·3	61·6	0·0361	0·0652	30·7	0·0025	0·0677	0·0132
Feb. 1 (3.0)	1·5	0·0824	330	35 ,,	94·2	58·2	0·0354	0·0648	36·0	0·0037	0·0685	0·0134
,, 2 (10.0)	2·0	0·0818	320	35 ,,	93·2	67·8	0·0348	0·0636	25·4	0·0026	0·0662	0·0129
,, 3 (10.0)	2·0	0·0812	290	36 ,,	93·7	62·2	0·0342	0·0625	31·5	0·0031	0·0656	0·0128
,, 4 (9.45)	2·3	0·0812	145	61 ,,	94·2	60·4	0·0342	0·0625	33·8	0·0020	0·0645	0·0126
,, 5 (9.30)	2·6	0·0806	145	61 ,,	92·5	63·0	0·0336	0·0614	29·5	0·0017	0·0631	0·0123
,, 7 (9.30)	2·5	0·0796	140	75 ,,	93·0	47·0	0·0326	0·0596	46·0	0·0022	0·0618	0·0121
,, 8 (9.30)	3·5	0·0794	10	900 ,,	89·0	46·0	0·0324	0·0592	43·0	0·0002	0·0594	0·0116
,, 9 (9.30)	5·0	0·0788	26	360 ,,	87·2	47·0	0·0318	0·0580	40·2	0·0004	0·0584	0·0114
,, 10 (10.0)	5·8	0·0782	33	270 ,,	84·6	47·7	0·0312	0·0571	36·9	0·0005	0·0576	0·0112
,, 11 (9.30)	8·5	0·0770	24	460 ,,	83·6	55·0	0·0300	0·0548	28·6	0·0002	0·0550	0·0107
,, 12 (9.30)	8·0	0·0762	48	185 ,,	89·0	50·0	0·0292	0·0533	39·0	0·0007	0·0540	0·0105
,, 14 (9.30)	6·5	0·0744	84	110 ,,	84·0	47·0	0·0274	0·0500	37·0	0·0012	0·0512	0·0100
,, 14 (3.15)	8·0	0·0743	80	140 ,,	80·4	45·4	0·0273	0·0498	35·0	0·0009	0·0507	0·0099
,, 15 (10.30)	4·5	0·0764	320	33 ,,	90·6	46·0	0·0294	0·0537	44·6	0·0048	0·0585	0·0114
,, 16 (10.0)	1·6	0·0790	320	33 ,,	91·0	42·0	0·0320	0·0586	49·0	0·0053	0·0639	0·0125
,, 17 (10.30)	4·0	0·0795	105	87 ,,	89·5	46·7	0·0325	0·0595	42·8	0·0018	0·0613	0·0120

It should be noted that the primary object of this investigation was to develop the apparatus for investigations of heat evolution by fruit, and, consequently, in these preliminary runs involving the use of apples, no attempt has been made to observe the various "controls" customary in physiological experiments.

It may be of interest to compute the gross magnitude of the quantities of heat involved in the case of a ship load of fruit. From the preliminary observations recorded in this Paper, it may be assumed that a cubic foot container of apples at a temperature of 20°C. generates heat at the rate of 0·14 calorie per second.

The refrigerating plant on a ship capable of carrying 100,000 bushel cases (=290,000 cu. ft. net insulated capacity) of apples would be from 100 to 150 B.H.P. The heat absorption capacity or coefficient of performance of such a plant is, according to tests, from 3 to 10, and theoretically could be as high as 50.* So, taking it as 10, it could remove an amount of heat from the hold which is the thermal equivalent of 1,500 horse-power.

From the data obtained in the present investigation, the heat evolution at a temperature of 20°C. from the 100,000 bushel cases of apples would be at a rate equivalent to 132 H.P., so that the heat produced by the process of respiration of the fruit would account for not less than 1/10th the duty on the machine.

Comparing the heat evolution by the apples with that conducted in through the insulated sides of the ship, it may be stated that the ratio of the heat evolution by the apples to the heat conducted in through the sides is as 1 is to 3.

This investigation was carried out on behalf of the Engineering Committee of the Food Investigation Board, and the author desires to record his thanks to Sir William Hardy, Director of the Board, for permission to publish this account. His thanks are also due to Mr. F. W. Morris, Junior Observer in the Physics Department, for his able assistance.

DISCUSSION.

Mr. J. H. BRINKWORTH suggested that the influence of humidity on rise of temperature would be affected in practice by the boxes and paper wrappings in which apples are stored.

Dr. A. H. DAVIS remarked that the author had painted both boxes dead black to ensure uniform emissivity. Did he suggest that the kind of paint made any difference at such temperatures?

Dr. C. CHREE asked whether any substantial heating effects occur in turnip and beetroot pits.

Dr. E. H. RAYNER pointed out that if research on fruit storage had not been set on foot, as a direct result of the war, importers would still go on losing occasional cargoes worth £100,000. He noticed that the temperature of the experiments was 20 degrees C. How did that compare with actual transport temperatures?

The Author, in reply, said that he had only considered the effect of humidity on the estimate of the heat produced: he had not investigated the effect which wrappings would have on temperature in actual transport. He admitted that black paint had no special virtue in the connection described, except that it provided an easily reproducible surface. He did not know much about the conditions in beetroot pits: his aim had been to provide an apparatus which biologists could use for inquiries into matters of that kind. The transport temperature was important, particularly in the tropics: he had chosen 20 degrees as the maximum which was likely to occur in practice.

* Lower temperature limit 5°C.; upper 10°C.

IX.—THE SCATTERING OF LIGHT BY INDIVIDUAL PARTICLES IN SMOKES.

By H. P. Walmsley.

Received April 21, 1927.

(*Communicated by* Dr. A. B. Wood.)

Abstract.

Applying the expression given by Maxwell for the number of collisions that occur between two sets of spherical uncharged molecules in a gas to the case of a smoke whose particles cover a wide range of sizes, it appears that particles of a given set collide less frequently with themselves than with those in sets of much larger or much smaller size. If the particles unite on contact, one would expect therefore that the units of the resulting aggregates would differ greatly in size. As this result is at variance with the deductions of Patterson and Whytlaw Gray from experimental data, the validity of their argument is discussed.

I.

In a recent Paper with the above title,* Patterson and Whytlaw Gray describe experiments from which they find that if the relation between the intensity of the light scattered by a particle and its radius be given by the empirical relation

$$I \propto r^n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

the experimental values of n for complex particles (aggregates) dispersed in air from mercury, silver and magnesium vary from 4·07 to 3·32. In discussing these results, it is assumed that if the packing of the units composing the aggregates is very loose, each unit will scatter light individually, and if the light scattered by any given unit is not screened by other units, the intensity of the scattered light I from the aggregate will be proportional to x, the number of units in the complex, and thus to the cube of the radius r, i.e.,

$$I \propto x \propto r^3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

With close packing and consequent screening, the incident light tends to be reflected from the surface of the complex, in which case the intensity becomes proportional to the surface, i.e.,

$$I \propto r^2 \propto x^{2/3} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

These are taken to be the two extreme cases, and they lead to values of n of 3 and 2 respectively.

Finding that the average scattering is more than proportional to the number of units in the complex—that is, the average scattering for each unit increases with the size of the aggregate—it is concluded that as the units themselves show a considerable range of sizes, the ones composing the larger aggregates consist of particles of larger average size than those constituting a smaller aggregate, "since the chance of large units combining to form a complex is the same as for small." The increased scattering by the larger units is called upon to explain the effect.

The conclusion seems unwarranted. If the disturbance at the point of obser-

* Proc. Roy. Soc., A. 113, p. 312 (1926).

vation due to a unit in the complex be represented by $\cos(pt-\varepsilon)$, that due to x units loosely packed is $\Sigma_x \cos(pt-\varepsilon)$. The intensity is therefore given by

$$I=(\Sigma \cos \varepsilon)^2+(\Sigma \sin \varepsilon)^2$$
$$=x+2\Sigma \cos(\varepsilon-\varepsilon') \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where the summation is taken over the $\frac{1}{2}x(x-1)$ phase differences between the units. This leads to equation (2) only when the distribution of the units makes the second term vanish. If the dimensions of the complex are small compared with the wavelength of the incident light, the second term clearly cannot be zero, for, as the size of the complex diminishes, $\cos(\varepsilon-\varepsilon')$ tends to the value unity for each of the $\frac{1}{2}x(x-1)$ phase differences, so I tends to the value x^2. Thus the scattering becomes in the limit proportional to r^6, as in Rayleigh's law. As the size of the aggregate increases from this limit, the general effect of the second term of equation (4) will make the average scattering for each unit decrease. Even where the units can perform independent internal random movements—a case where the statistical average value of the second term is a minimum—it would be necessary for the dimensions of the complex to be of the order of the wavelength of the incident light before I becomes proportional to x. Hence, as r increases from zero, the index n of the empirical equation (1) should diminish from the value six to the value three.

With close packing and consequent screening, the light ultimately tends to be scattered from the surface units, and in the limiting case, where the second term of equation (4) vanishes, it becomes proportional to the number of particles on the surface—i.e., to r^2. Thus excluding special distributions of the units, we should in general expect n to range between six and two for these ultramicroscopic particles.

The experimental values for particles from the different dispersoids examined decreased in the order—mercury ($n=4{\cdot}07$), silver ($n=3{\cdot}97$), magnesium oxide ($n=3{\cdot}32$). As the average sizes of the particles examined in each case increased in this order, the results apparently conform with theory. The values for silver ($n=3{\cdot}97$) and mercuric chloride ($n=2{\cdot}10$), where the average range of sizes was about the same, show the influence of the packing on the value of n. As Patterson and Whytlaw Gray point out, this seems confirmed by their density measurements, the silver aggregates having about one-tenth the normal density, whereas the mercuric chloride aggregates have about one-quarter the normal density.

This result, of course, makes it difficult to apportion the relative effects of size and packing on the values of n in the above series. However, as a relation between n and r was actually looked for in each experiment and, "except in one or two doubtful cases, no evidence whatever was obtained that the value of n varied appreciably over the range of size considered within the limits of experimental error," it would appear that the relative effect of packing was the dominant factor influencing the values of n in the series. Two factors may contribute to the negative experimental result. Equations (2) and (3) pre-suppose a uniform distribution of units throughout the aggregate. If, as is highly probable, the aggregates are skeleton crystal growths about a nucleus, the density of the units will diminish radially from the nucleus. As the outer units are the more effective in producing interference, the value of I (equation 4) will diminish less rapidly with the radius than it would if the distribution were more uniform. The radius in this case we will take as equal to that of a circumscribing sphere. Since the experimental values of r are deduced from the Stokes-Cunningham law, they can hardly be expected to

agree with the radius of the circumscribing sphere, and it may happen that the values so obtained accentuate the former effect and produce the observed negative result. A radial diminution in the density of the units should cause the mean density of the aggregate to diminish as the size increases. The measured sizes and densities of individual aggregates* seem to show this tendency in the cases of silver and magnesium oxide, but the number of observations quoted is too small to establish the point.

Taking into consideration the sizes of the particles examined (their radii ranged from $130\mu\mu$ to $1600\mu\mu$), the fact that the average scattering for each unit of a complex particle may increase with the number of units (i.e., when $n > 3$) is not, of itself, sufficient to prove that the average size of the units is greater in large than in small complexes. It can be due to vibrations from the individual units arriving at the point of observation in phase.

II.

The distribution of size amongst the units of an aggregate must, to a large extent, be governed by their collision frequencies before aggregation. Maxwell† has given an expression for the number of collisions that occur in unit time between two sets of spherical particles, from which it appears that the number of occasions per unit time in which two spherical units of radius r and r_1 come into contact is $\pi(r+r_1)^2\sqrt{u^2+u_1^2}\,.\,\rho\rho_1$, where u and u_1 are their velocities and ρ and ρ_1 the numbers per unit volume. Assuming the densities Δ are equal, and that the kinetic energies of the particles are the same as the mean kinetic energy E of a gas molecule of the surrounding medium, we have

$$\tfrac{1}{2}\times 4/3\times\pi r^3\Delta\times u^2=E$$

Eliminating the velocities of translation, the number of collisions becomes proportional to

$$(1+p)^2\,(1+p^{-3})^{\frac{1}{2}}\,.\,\sqrt{r} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where $p=r_1/r$. For a sphere of given size this quantity becomes very great for both relatively small and relatively large values of p, and has a minimum value close to $p=0{\cdot}8555$. From this it is evident that, where an extensive size range exists, a given particle is much more likely to collide with a particle of larger or much smaller size than with one of its own size, and, owing to the presence of the factor $\sqrt{r}$, this tendency increases as the size of the particle increases. If the particles unite at contact, one would not therefore expect the units of the aggregates to consist of particles of fairly uniform size, but rather the reverse, and this is in effect the impression one obtains when they are examined under the microscope. The string-like aggregates produced by CdO and ZnO consists of units of various sizes linked together. When seen by oblique illumination, the increased scattering due to the larger units causes the chains of particles to appear like beads on a thread; often as if they were separated from each other by a small space. The spaces occur where the units are of too small size to scatter an appreciable amount of light. The combination of large and considerably smaller particles in many aggregates is also evident in the photomicrograph of a deposit from a magnesium oxide smoke published with the Paper of Patterson and Whytlaw Gray. It has been adapted in the construction of the models of the previous Paper.

* Loc. cit., p. 307.

† J. C. Maxwell, Phil. Mag. (4), 19, p. 28 (1860); Collected Papers, Vol. 1, p. 387.

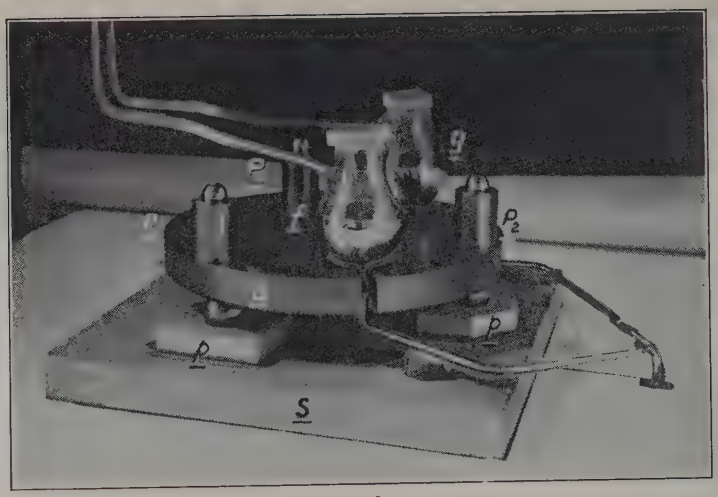


FIG. 1.

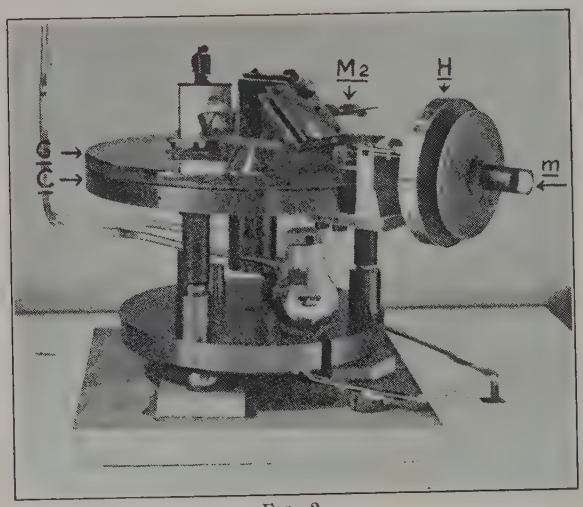


FIG. 2.

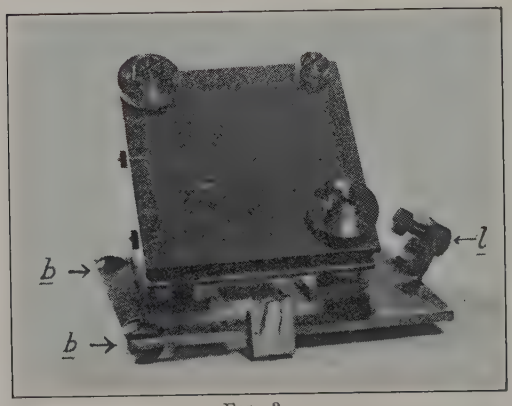


FIG. 3.

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X.—ON THE CONSTRUCTION AND STANDARDIZATION OF AN INTERFEROMETER PRESSURE GAUGE.

By J. J. Manley, *M.A.*, Research Fellow, Magdalen College, Oxford.

Abstract.

This Paper deals with the application of a Michelson interferometer to the determination of gas pressures ranging from 0·0001 to 20 mm. of mercury. The construction of the instrument is fully described as are also the methods used for standardising the registering micrometer screw and its graduated head. The gauge can be instantaneously set and the pressure which obtained at the moment of setting measured at leisure.

THE gauge dealt with in this Paper, although applicable for the measurement of small pressures in general, was primarily designed for determining the rate of the electric eruption of any gas-grown skin found upon the interior surfaces of highly evacuated vessels. A chief merit of the instrument lies in the fact that, unlike some gauges, it can be instantly set at any given moment and then read at leisure. Briefly, the gauge is a Michelson interferometer, in which the usual vertical mirrors of silver-upon-glass have been replaced by two horizontal surfaces of mercury. These mercurial surfaces are the summits of two similar barometric columns, one of which is used as a standard of reference for the other. The gauge, which was carried by a large and massive slate bench cemented to concrete pillars, was constructed as follows.

Upon a marble slab S (Fig. 1), supported by three lead pellets for ensuring stability, were placed three marble plates, each having a cavity for the reception of a 1″ steel ball. Two of these plates, p, p, with their balls, are shown in Fig. 1. The plates were so disposed that the balls coincided with the apices of an equilateral triangle, and respectively engaged the hole, slot and plane of the under surface of a heavy brass disc B. The legs of a second massive disc C (Fig. 2), terminated respectively in a hole, a slot and a plane; and these, with C *in situ*, rested upon corresponding steel balls carried by the pillars P_1, P_2, P_3, shown in Fig. 1. The disc C (Fig. 2) was covered with a thick glass plate G, upon which were built the *ways* required for two radial slides, each carrying a plane mirror. Each way was formed by cementing to G two plane glass plates, the one being vertical and the other set at an angle approximating 45°. All four plates were buttressed. The brass slides running in the ways were each fitted with 2 steel balls b, b (Fig. 3), and an adjustable support l, the arrangement being such that the balls made contact not only with G, but also with the vertical plate of the way. The support l had contact with the sloping plate only; the contact system was therefore one of five points. Hence, given accurately prepared ways or guides, the slides with their mirrors run true. The plane mirrors carried by the slides were mounted and adjusted after Michelson's plan, but instead of being vertical they were inclined downwards through an angle of 45°. The two beams of light emanating from the half-silvered plate of the interferometer were by these inclined mirrors reflected downwards through radial slots cut in the discs C and G. Thus, one beam impinged upon the surface of the standard

mercury column (*vide infra*), and the other upon that of the column responding to an introduced gas. The slides were controlled by elastic bands, and actuated by micrometer screws having a pitch of 0·5 mm. The screws terminated in fine and extremely hard points, and these were made to bear upon glass plates cemented to the slides. One screw M_1, termed the working micrometer, was fitted with a large head H (Fig. 2), having a scale of 600 divisions which were viewed with a micrometer microscope. Any traverse of the screw could be read to within 1/10th of a division—that is to say, the limit of accuracy attainable in reading was approximately $\frac{0{\cdot}5}{600\times10}=0{\cdot}00008$ mm. The second micrometer screw M_2, termed the compensator, was left unmodified and used as received from the makers, Messrs. Pye & Co., of Cambridge. The smallest division upon its head=0·005 mm. The half-silvered parallel-plane glass plate used for dividing the beam of light, and also the compensating plate of the interferometer, were mounted in the usual way, and definitely located upon the base-plate G.* For maintaining uniformity of temperature within the instrument the upper part was enclosed by an aluminium wall and cover, and the lower portion surrounded by asbestos millboard, as seen in Fig. 4. The incident and reflected beams of light were transmitted through glazed windows in the aluminium wall. A brief description may now be given of the twin barometric columns and of their disposition.

In Fig. 1 are shown two flasks f, g,† which rest in leather-lined conical holes made in B. The mouth of each was turned in and given the form of a flat sloping ring with an aperture of 12 mm. The rings were ground true and then closed by parallel-plane glass plates attached with Canada balsam. Each flask had two tubes, the one leading out from the neck and the other from the bottom. One of the two side-tubes was joined to a Sprengel pump and the other to a second pump, and also to any apparatus to be evacuated. The second or vertical tube constituted in each instance the upper portion of a barometric column, terminating in the flask with its wide surface of mercury. These twin barometric tubes were bent and led side by side through a hole in the slate bench, and finally fused, the one to E and the other to F, as shown in Fig. 5. The lower ends of the cisterns E and F were placed in cavities in a block W. By means of the stop-cocks t_1 and t_2 communication between the two barometric columns and a main wooden cistern T could be established or broken at will. An auxiliary cistern N was added, so that the mercury in T might be varied with ease. Any desired level of the adjusted mercury was maintained by closing the tap t_3. Equality of temperature within and about the barometric tubes and their cisterns was secured by completely surrounding them with a case of wood and asbestos. The short exposed portions of the two columns seen close to the plate B in Fig. 1 were finally wrapped in asbestos fibre.

Before using the gauge, the scale upon the head H of the working micrometer, and also that portion of the screw traversing the nut when measuring the major pressure of 20 mm., were calibrated according to the methods detailed below.

(*a*) *Calibration of the Micrometer Head H.*—To aid in determining the errors of the scale upon H, the spindle protruding from the centre was fitted with a small wooden cylinder, which could be rotated and clamped as required. The anterior

* A plan view of the gauge is given in Fig. 6.

† The diameter of these was 5 cm.

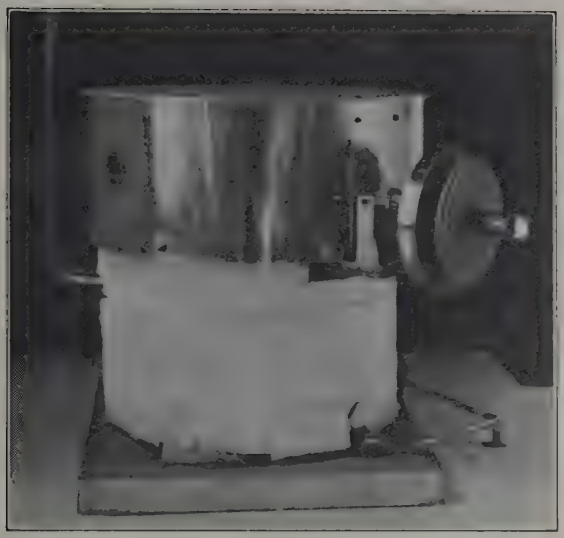

FIG. 4.

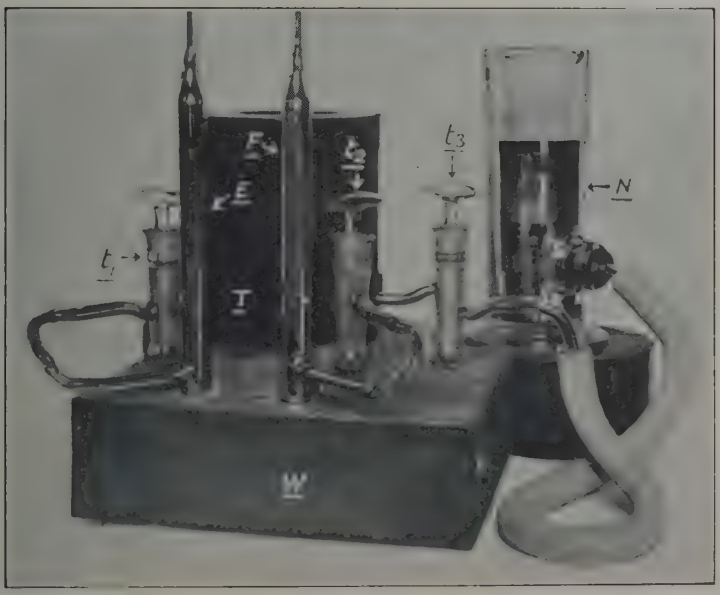

FIG. 5.

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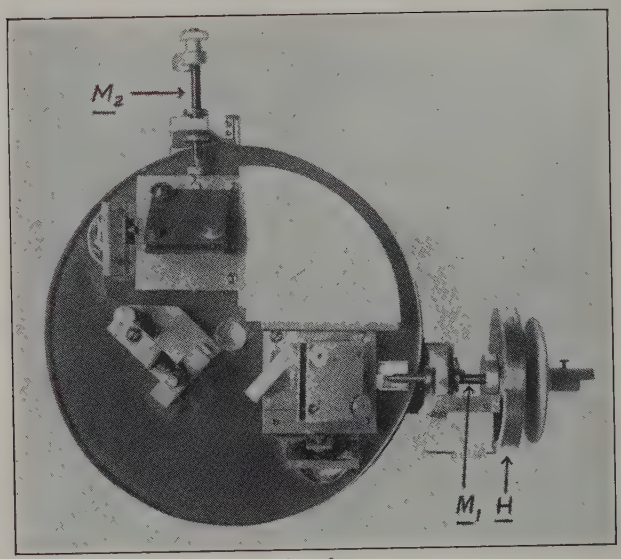

FIG. 6.

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portion of this cylinder was cut along its axis and one half removed ; and to the central flat surface thus provided was secured a concave mirror m (Fig. 2). Opposite the mirror, and at a distance of 2 m. from it, was placed a vertical mm. scale ; also a lamp having a rectilinear filament. These preliminaries ended, the errors of H were determined as follows.

First, the zero of the scale was set to coincide with a cross-thread of the reading microscope. Next, m was adjusted and clamped so that the image of the filament was near the top of the vertical scale and a first reading r_1 taken. H was then turned until the sixth instead of the zero division of its scale coincided with the cross-thread, and a second reading r_2 taken. A measure $r_2 - r_1$ was thus obtained for the first portion of the scale having the indicated value of 0·005 mm.

For the next step, the micrometer was left undisturbed, whilst the mirror was returned to its original position, or approximately so, and a new deflectional reading obtained. Then, following the plan just described, the next 0·005 mm. was calibrated. Proceeding thus for 100 steps data were obtained for standardizing the whole scale. The calibrated steps were found to vary within the limits of $\pm 1{\cdot}6$ per cent.

As illustrating the degree of accuracy here attained, it may be stated that, in a series of determinations for one and the same step giving a mean deflection of 257 mm., the greatest variation was ± 1, or $\pm 0{\cdot}39$ per cent. The errors of the micrometer head having been ascertained, it was then possible to standardize the screw itself. This was done as follows.

(*b*) *Calibration of the Screw.*—For calibrating the working screw M_1 the interferometer was first adjusted for the fringes obtained with a sodium flame, and the reading of M_1 made equal to zero. Then the compensator M_2 was manipulated so that one fringe was accurately sighted. Next M_1 was slowly turned until x fringes had crossed the fiducial line, and then by means of its micrometer microscope read a second time. Knowing x, the *apparent* distance traversed by the screw was therefore $0{\cdot}000589 \, . \, x$ mm. It will, however, be noted that with the advance of the screw the paths of the incident and reflected beams were simultaneously and equally shortened. Hence the *real* traverse was $0{\cdot}000589 \, . \, x/2$ mm. This known, the error in the first region is determinable.*

For the actual calibration, the plan adopted was that in which a portion of the screw corresponding to 0·005 mm. was tested in the neighbourhood of each successive 0·25 mm. division throughout the whole required range of 10 mm. ; the number of calibrated regions thus being 41. By taking $x = 17$, the standard length was $0{\cdot}000589 \, x \times 17/2$ mm., a quantity differing from a compared length of 0·005 mm. by $+0{\cdot}1$ per cent. only.

The error of the first region having been determined, M_1 was advanced 0·25 mm. and an accurate reading taken. Then, as already described, the coincidence of a fringe with the cross-threads of the telescope was effected by means of M_2. Lastly, M_1 was again turned until the standard number of fringes had crossed the threads of the telescope, and a further reading taken. From the data thus acquired the error for region 2 of the screw was calculated. Proceeding thus, the standardisation was completed, and a table of corrections prepared for future use. It was found

* When standardizing M_1, plane silver mirrors may be substituted for the mercurial surfaces of the barometric columns. If this be done, the calibration is not interrupted by passing tremors.

that the mean errors of $M_1 = \pm 3{\cdot}2$ per cent. For the sake of clarity, an example of the method of using the gauge may now be given.

Determination of the Pressure of a Gas.—First, communication between the two barometric tubes is established by opening an intervening mercury trap not shown in the figures. Both pumps are then brought into use and the system evacuated to the highest attainable degree. This done, the mercury in the cistern T is varied by operating the auxiliary cistern N until the upper and common level of the mercurial columns coincides approximately with the centres of the flasks f, g. The stopcock t_3 is then closed, and subsequently, at one and the same moment, t_1 and t_2 are also closed. Thus, for the time being, the two barometric columns, having one and the same length, are rendered invariable. Next, for the sodium flame used in standardising M_1 is substituted a 40 W. "Fullolite" lamp, and M_1 set at or just within the zero of its scale and its position a_1 read. Then M_2 is adjusted so that the central band of the coloured interference fringes appears upon the fiducial line of the telescope. Finally, the trap between the barometric columns is closed, t_1 and t_2 opened, and the gauge thus made ready for use.*

If now any small quantity of gas be generated within an apparatus attached to the barometric column of M_1, the mercury will be correspondingly depressed and the optical path associated with it lengthened; the fringes will therefore move across the field and probably disappear. The micrometer M_1 is then slowly turned and the central fringe restored to its original position. Thus the optical path is shortened by precisely the same amount as by the pressure of the gas it was lengthened. Let the new micrometer reading be a_2. Then, since the incident and reflected rays are equally shortened, the actual pressure of the gas is $2(a_2 - a_1)$ mm. With a little experience M_1 can be adjusted to within 2/10th of a fringe; hence the pressure values are determinable to within 0·0001 mm.†

If it be necessary to apply a correction for the temperature of the mercurial columns, the required data may be obtained in the usual way by thermometers appropriately placed. Since, however, the *difference* in the height of the intimately associated twin columns is never greater than 20 mm., the correction will in general be small, and in most cases may be altogether neglected.

It will be obvious that a series of sufficiently small gas pressures may be measured either individually or differentially, the latter being the more expeditious.

In conclusion, it must be said that the gauge can be used only in the complete absence of vibration. Any small tremor gives rise to ripples upon the mercurial surfaces, and a consequent distortion of the fringes. But given tranquil conditions, pressure measurements may be carried out quickly and with ease.

DISCUSSION.

The Author, in presenting his Paper, added that he hoped to overcome the difficulty arising from ripples on the surface of the mercury by floating on it thin slips of glass, which, unlike thicker strips, keep to the middle of the mercury surface. He also explained two simple methods of making optically perfect mirrors (Phil. Mag., January, 1928).

Prof. O. W. Richardson asked what degree of sensibility could be obtained with the apparatus, and whether the temperature errors were serious.

* The standard barometric tube working in conjunction with M_2, having been trapped off, is kept highly evacuated by ceaselessly working the pump with which it communicates.

† The two barometric columns, although continuously responding to atmospheric pressure, are *simultaneously and equally* affected. Hence the differential readings are not invalidated.

The AUTHOR replied that readings could be taken to 0.1μ, and that temperature errors were compensated by the differential use of two similar mercury columns.

Mr. R. S. WHIPPLE congratulated the author on having worked out a very elegant piece of apparatus. He suggested that instead of glass slips small mirrors made of rustless steel might be floated on the mercury. This plan would be free from difficulties due to bubbles. He had found that results reproducible to 1μ could be obtained by the simple method of measuring displacements of a mercury or oil surface which consists in bringing down a point till it touches the surface. How long did the observations take ?

The AUTHOR replied that the time taken by the observations was merely that needed to set the micrometer screw.

Mr. T. SMITH asked whether the author employed fringes running in any special direction (for instance, vertically). Had he investigated whether one direction was theoretically preferable to the others ?

The AUTHOR replied that he preferred vertical fringes which move laterally, as a matter of convenience. He thought that errors of the kind which might make one direction preferable to another would be balanced out by the method of calibration. Also, the observed fringes being arcs of equally spaced concentric circles, it is possible to select and use either horizontal or vertical portions. Theoretically, the value of a measurement is the same for both horizontal and vertical fringes.

Dr. D. OWEN expressed great interest in the apparatus. Owing to its somewhat elaborate construction it was hardly suitable for universal use, but could not the author compare its readings with those of a McLeod gauge ? One of the light pencils in the interferometer has to pass through the film of air adsorbed on the surface of the mercury, while the other does not. Would it not be possible, by a comparison of the kind suggested, to find evidence as to the nature of this film ?

The AUTHOR replied that if, as stated by Langmuir, the gas skin was only 1 molecule thick, it could hardly be detected. If, as he believed, the skin was about 20 molecules thick, he did not know whether its detection would be possible by the method suggested by Dr. Owen. His gauge measured the actual pressure, whereas in the McLeod gauge the changes of pressure would presumably cause changes in the amount of gas adsorbed on the containing walls and so would give rise to errors.

Mr. D. H. BLACK asked why the author took the displacement of the mercury to be double the compensating displacement of the micrometer mirror, since the light pencil has to traverse twice the increment of path to which the displacement of the mercury gives rise ? He suggested that, instead of using two manometers both open to the air, the author might use one manometer with a closed end containing a vacuum, and replace the other mercury surface by a fixed mirror.

The AUTHOR replied that the object of using two manometers differentially was to compensate for variations in temperature and atmospheric pressure. If the level of the comparison surface be fixed by closing the appropriate tap a constant movement of the fringes can be observed.

XI.—THE DIELECTRIC CONSTANT OF LIQUID BROMINE.

By Anne I. Anderson, *B.Sc.*

Received November 22, 1927.

Abstract.

An account is given of a re-determination o the dielectric constant of liquid bromine, the value found being 3·12 at 15°C., and at a frequency of 187,000 per sec., with a temperature coefficient of −0·00191 referred to 0°C. Applying the dipole theory of Debye and Gans to the results, a value of $0{\cdot}40 \times 10^{-18}$ is deduced for the electric moment of the bromine molecule Br_2. The electrical conductivity was also measured.

Introductory.

DETERMINATIONS of the dielectric properties of a limited number of liquids have recently been made by various experimenters with a view to testing Debye's well-known theory, elaborated by Gans and Isnardi to include liquid dielectrics. The theoretical side has been well summarised by Prof. Compton in his address on "Dielectric Constants and Molecular Structure."*

Liquid bromine, being an element, should be helpful in this respect; but it has recently received little attention, doubtless owing to the experimental difficulties of dealing with it.

Previous published determinations of the dielectric constant of liquid bromine are as follows:—

Author.	Date.	ε	t	λ
Schlundt	1901	3·18	23°C.	84 cm.
Schmidt	1903	3·10	...	...
Walden	1910	4·6	1°C.	"∞" (i.e., $>10^4$cm.)

Drude's "second" resonance method was used. The first mentioned determination alone seems to merit serious consideration.

Schlundt and Eggers estimate the limit of error for this method at as much as 2 or 3 per cent., while none of the above workers record observations either upon the temperature coefficient of the dielectric constant or upon the electrical conductivities of the samples used.

Hence the opportunity of making a fuller and more accurate re-determination of the dielectric constant was taken when a sample of specially purified and dried bromine was kindly placed at my disposal by Prof. H. B. Baker. It is not claimed, however, that the liquid upon which the tests were carried out was of the extraordinary degree of dryness of the sample as first supplied. Exposure to the air for a brief period, in the course of transference to the testing vessel, was inevitable. The bromine was introduced into a glass bulb *A* (Fig. 1), containing specially

* Science, 63, pp. 53-58, January 15 (1926).

purified phosphorus pentoxide. After sealing off, the bromine was allowed to stand for three weeks. It was then distilled over into the test condenser *B*, which was immersed in a freezing mixture. A mercury seal was used above the glass stopper of the condenser vessel.

Determinations of the dielectric constant and its temperature coefficient were

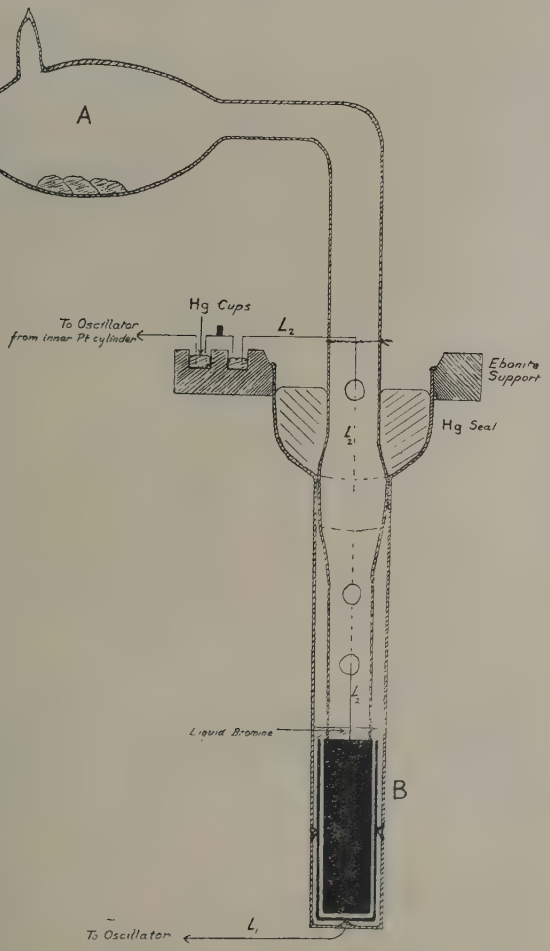

FIG. 1.—BROMINE CONDENSER.

then carried out upon this sample ; measurements were also made of the electrical conductivity at different temperatures (with due regard to polarisation effects exhibited), and the density and its temperature coefficient were observed. The effect of frequency on the dielectric constant was also examined.

The Determination of the Dielectric Constant.

The method adopted has been employed by other experimenters, and is shown in Fig. 2. Two generators of H.F. oscillations produced a heterodyne note in a third detector circuit operating a loud-speaker. The first generating circuit consisted of a Sullivan wave-meter, oscillating at a set frequency. The second circuit included two variable air condensers, C_1 and C_2 (0·001μF. max. and 100$\mu\mu$F. max.), and the experimental condenser, C_3, containing the bromine; these three condensers being connected in parallel across the grid circuit. The generating circuits were lightly coupled to the detector circuit. Fig. 1 is a drawing of the vessel used as a condenser. The vessel consists of a piece of glass tubing, ground, at a distance of 13·5 cm. from its lower end, to form a hollow stopper to an outer glass tube closed at its lower end. Fitting tightly over the inner glass tube is a platinum sleeve, 5 cm. long, with platinum base. This sleeve is surrounded by a hollow concentric platinum cylinder—also closed at its lower end—which is fixed rigidly to the outer glass tube. These two cylinders, separated by a space about 1 mm. wide, consti-

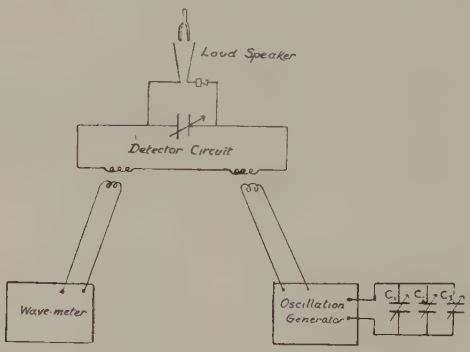

Fig. 2.—Diagram of Electric Circuits.

tute the plates of the condenser C_3 of Fig. 2. Platinum wire electrodes, L_1 and L_2, are led off from each cylinder as indicated. The method of introducing and removing the bromine from the condenser has already been described.

After the 100$\mu\mu$F. variable condenser had been adjusted so that the note in the loud-speaker made very slow beats with a tuning fork of frequency 768, the corresponding condenser scale readings, *a*, *b*, *c* and *d* for the following conditions, were observed:—

(*a*) When the experimental condenser, filled with bromine at a known temperature, was connected in the circuit;

(*b*) When the experimental condenser was disconnected by means of a small key;

(*c*) When the experimental condenser, with the bromine removed and air as dielectric, was re-connected in the circuit;

(*d*) When the experimental condenser was again disconnected.

When these readings have been corrected by the condenser calibration curve,

and allowance has been made for the capacity of the fine wire lead L_2, the dielectric constant is given by

$$\varepsilon = \frac{b' - a'}{d' - c''}$$

where a', b', c', d' are the corrected values of the readings a, b, c, d.

This is a ratio and is independent of the actual value of the units in which the capacities were measured.

To minimise stray capacities, the observer and loud-speaker were situated at a distance of about 2 metres from the apparatus, and the 100$\mu\mu$F. condenser was operated from this point by means of a horizontal dial rotating a belt of fine silk cord. All observations were made on the same side of the wavemeter frequency. Care was taken to ascertain that the drift of frequency of the generators was negligible over the duration of a measurement. The filaments in the two generating circuits were connected in series, and, with a common high-tension battery of about 60 volts, the frequencies of oscillation became steady some 20 minutes after closing the circuits. The heterodyne note, when adjusted to the frequency of the standard fork, then remained constant to within two beats per second for at least a couple of minutes. In taking readings, the rate of beating was adjusted so as to be well within two beats per second. A change of this amount corresponds to an alteration in capacity of at most 1 in 44,000, hence the errors of adjustment of frequency were quite negligibly small.

The limit of accuracy in the measurement is essentially determined by the degree of constancy, at the various points of its scale, of the 100$\mu\mu$F. condenser which was substituted for the test condenser when the latter was cut out of circuit. This condenser could be read to 0·015 $\mu\mu$F. by the aid of a long ebonite pointer moving over a scale mounted on a marble base. It was calibrated by the aid of a small fixed parallel plate air condenser (5 $\mu\mu$F. approx.), which could be either connected in parallel or disconnected by a small double-pole key. Readings were taken at short intervals along the scale, and a calibration curve was drawn to a large scale, whence differences of readings were tabulated in arbitrary units of capacity. This laborious operation of calibration and reduction of results to the form of a curve was repeated several times in the course of the measurements. The air capacity of the vessel was about 20$\mu\mu$F., and the pointer readings should, with perfect reproducibility, have given this value correct to 1 part in 1440. Actually, however, the lack of exact reproducibility of the 100 $\mu\mu$F. condenser was quite appreciable, the effect being to reduce the accuracy of the final determination of the dielectric constant to $\frac{1}{4}$ per cent.

When the readings with bromine had been taken, the bromine was redistilled back into A, and allowed to cool. The capacity of the condenser, with air as dielectric, was then observed. No appreciable alteration in the air capacity was detected after the vessel had been opened and cleaned and finally re-assembled. A slight chemical action appeared to have occurred at the electrodes, forming a very fine film on the platinum—presumably of platinum bromide, insoluble in bromine. The thickness of the film was quite insufficient to affect the thickness of the dielectric sensibly.

The main measurements having been completed, the capacity of the platinum lead, L_2, was determined directly in the same way, the lead being cut, for this purpose, immediately above its connection to the inner platinum cylinder. This

capacity amounted to 1·84 arbitrary units, as compared with 39·50 units for the air capacity—that is, to about 5 per cent. of the air capacity of the test condenser. This has to be subtracted from each of the capacities $b-a$ and $d-c$.

Theoretically the effective capacity of the bromine condenser is affected by the electrical conductivity of the bromine. Calculation shows that the effect of this shunt is to cause a virtual drop in capacity of about one part in a million; the effect is thus negligible.

The above experiments gave the value **$3{\cdot}11_9$ for the dielectric constant of liquid bromine at 15°C. and at a frequency of 187,000 per sec.**

At the same temperature, but at a frequency of over a million per sec., no variation exceeding 1 in 350 could be detected in the dielectric constant. The dimensions of the vessel did not permit of an accurate determination at audio-frequency.

Temperature Coefficient of the Dielectric Constant.

A determination of the temperature coefficient of the dielectric constant was made at a frequency of 187,000 per sec. Readings were taken at a temperature slightly above 0°C. (by placing the condenser in a container filled up with melting ice) and also at the practically steady temperature of the laboratory. The values obtained were

$3{\cdot}20_6$ at 1·02°; $3{\cdot}13_1$ at 13·4°; $3{\cdot}12_3$ at 14·4°; and $3{\cdot}10_3$ at 17·65°C.

When these observations are plotted it is found that, for this small range, ε_t (the D.C. at t°C.) may be expressed by the linear relation $\varepsilon_t=\varepsilon_0(1+\alpha t)$ where ε_0 (the D.C. at 0°C.)$=3{\cdot}212$, and $\alpha=-0{\cdot}00191$ per degree Centigrade. This value of the temperature-coefficient is in very close agreement with the results of measurements made six months earlier on the same sample of bromine.

Electrical Conductivity.

The resistance of the bromine between the condenser electrodes was observed at various temperatures by measuring the current when a steady voltage was applied to the condenser in series with a high resistance galvanometer. Polarisation effects were observed, and readings were accordingly taken of the growth and decay of the galvanometer deflections with time after each reversal of the sign of the applied electromotive force. The maximum deflection observed was adopted as representing the true conductivity. The variation of readings with time is illustrated in Fig. 3. The vessel was calibrated by substituting a 1/100 N solution of KCl and determining its resistance by an A.C. bridge at audio frequency. The resulting value of the electrical conductivity was $9{\cdot}6\times10^{-10}$ ohm^{-1} cm.$^{-1}$ at 0°C., with a temperature coefficient of −0·0188 per degree Centigrade. The actual resistance of the bromine was $5{\cdot}46\times10^6$ ohms at 0°C.*

Electric Moment of the Bromine Molecule.

A careful examination of the results of the above experiments shows that the Clausius-Mosotti relation $(\varepsilon-1)/(\varepsilon+2)D=$constant (where $D=$ density) is not satisfied, this function falling unmistakably with rise of temperature. On the theory of Debye, and its extension by Gans, this decrease in $(\varepsilon-1)/(\varepsilon+2)D$ with

* The conductivity of liquid bromine has recently been investigated by Rabinowitsch (Zeit. Phys. Chem., 119, February, 1926), who records observations on samples under different conditions.

rise of temperature indicates the presence of dipoles or electric doublets. It is, therefore, of interest to deduce the value of the electric moment of the Br_2 molecule.

Using the formula

$$(\varepsilon-1)/(\varepsilon+2)D=A+B/T$$

(where A and B are constants and T denotes the absolute temperature), the electric moment is obtained by the relation $B=4\pi N\mu^2/9kD$, where N=number of molecules per c.c., μ=the electric moment and k=Boltzmann's constant ($1{\cdot}372\times10^{-16}$).

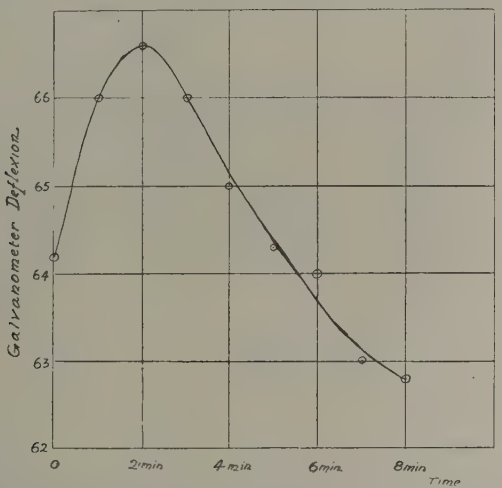

FIG. 3.—POLARISATION EFFECTS IN LIQUID BROMINE RESISTANCE.

On substituting experimental results from this Paper, the value $B=6{\cdot}3$ ($\pm0{\cdot}7$) is deduced.

The determination of B involves the determination of the density, D, and its variation with temperature. Since no modern data appeared to be in existence as to the density of liquid bromine at 0°C., this determination was made, and a mean temperature-coefficient of $-0{\cdot}00104$ was found over the range 0°C.— 20°C.,* this value being used in the calculation of B. It should be noted, however, that the percentage accuracy of the deduced value of B is lower than that of the determination of the dielectric constant, or rather of $(\varepsilon-1)/(\varepsilon+2)$.

Taking $1{\cdot}64\times10^{-24}$gm. for the mass of the hydrogen atom, the electric moment of the bromine molecule Br_2 is found to be

$$\mu=0{\cdot}40(\pm0{\cdot}04)\times10^{-18}.$$

Cordial acknowledgment is made to Mr. G. L. Addenbrooke, at whose suggestion the work was undertaken and who kindly provided the condenser vessel already constructed to his design. The experiments were carried out at the Sir John Cass Technical Institute, London, under the direction of Dr. D. Owen, who kindly filled the vessel with bromine and for whose valuable help I am greatly indebted.

* Cf. with the value $-0{\cdot}0011$ given in the Int. Critical Tables over the range 0°C.— 30°C.

DISCUSSION.

Prof. O. W. RICHARDSON said that he was surprised to find such a high estimate of the electric moment of the bromine molecule. That given by the author was of the order of the product of the electronic charge and the diameter of an atom.

Mr. L. HARTSHORN congratulated the author on having obtained a reliable value of the dielectric constant in the case of such a difficult substance as bromine. Some time ago he had had to examine the published values of some 200 dielectric constants, and had found reason to believe that many of them were affected by very large sources of error, most of which the author had avoided. He thought, however, that she was optimistic in taking her result to the third decimal place. The main error would arise from the difficulty in measuring a small capacity accurately: the accuracy would be that of the smallest (20 $\mu\mu$F.) condenser, and although the author had used a single disconnection in the leads of the experimental condenser (thereby avoiding the errors introduced by a double disconnection), still, errors would arise from cross capacities between the leads and also from the capacity between the separated contacts of the disconnecting switch; thus between mercury cups in ebonite a capacity of 1 $\mu\mu$F. is not uncommon. These residual capacities would not be the same when the dielectric in the experimental condenser was bromine as when it was air. He did not think an accuracy of more than 1 per cent. was attainable in such measurements without the use of the elaborate bridge he had described to the Society three years ago. As regards the electric moment of the molecules, that obtained for bromine was about half as great as that of ethyl ether, and so seemed improbably high. The small temperature coefficient from which it had been deduced was partly due to change in density, and the small residuum ascribable to the presence of dipoles was not ascertained with sufficient accuracy or based on sufficiently numerous observations to justify the assumption of a linear relation between temperature and dielectric constant. He thought that the author's value of the electric moment could not, therefore, be relied on.

Mr. D. H. BLACK: Over 18 months ago, in connection with some research on the D.C. properties of insulating oils upon which I have been engaged for some considerable time, I observed that an oil gives a similar current-time curve to that shown in Fig. 3, the time to rise to a maximum varying according to the nature and the condition of the oil. I fail to see how such a curve can be explained as being due to polarisation as mentioned in the Paper, for on reversing the applied E.M.F. the polarisation E.M.F., which had previously been in opposition, would now be assisting it, thus causing a larger current to flow than that which would be due to the applied E.M.F. alone. This latter current can be observed on the initial application of the voltage after the film of oil has been short-circuited for some hours, and it is found to decrease from the moment of application. My own opinion is that the observed facts are due to the formation of a contact resistance on one or both of the electrodes similar to that observed when dealing with ordinary electrolytes. Such an assumption gives a very simple explanation of the observed facts, for on reversing the applied E.M.F. the contact resistance which had been formed would take time to disappear, and at the same time a similar resistance would be built up on the opposite electrode, giving the rising and the falling portion necessary to give such a curve as Fig. 3. Polarisation electromotive forces may be present, but in the case of oils, at any rate, their effect is small in comparison with the effects of the contact resistances. This theory is strongly supported by other experiments which I have carried out on various oils, and it gives a simple explanation of many of the apparent anomalies met with when making electrical measurements on liquid dielectrics.

Mr. G. L. ADDENBROOKE: Miss Anderson mentions that the condenser vessel for these experiments was provided by me and that the work was undertaken at my suggestion. It may, therefore, add something to the value of the Paper if I mention something of my preliminary work on the subject. In a discussion at the last meeting of the Society I sketched a diagram dealing with the electrical properties of celluloid, since reproduced in the Society's Bulletin. The experiments on celluloid were made in 1916. To pursue the matter further, I began to look out for some less complicated substance. With this view, I consulted the late Sir James Dewar, when he expressed the view that for scientific purposes experiments on substances of definite chemical composition were the only ones of value, and suggested work on crystals. There are a good many difficulties, however, in working with crystals, and after consideration of these and the cost, I was deterred from pursuing the subject in this form, because such crystals would be formed of at least two elements with their water of crystallisation. It seemed to me, therefore, that it would be more fundamental, if possible, to begin by a study of the electrical

properties of the dielectric elements themselves as far as they could be obtained, free from impurities, and especially moisture. This would thus form a basis for the study of composite substances later. With this view, I looked up the available data regarding the non-metallic elements, and ultimately found the capacity of 10 elements, including liquified gases, were quoted in recent tables of physical constants, and that they were in general agreement with the squares of these refractive indexes. Amongst these elements were chlorine, bromine and iodine. I was particularly desirous of knowing, also, the electrical resistance of all the elements and their losses in alternating fields as showing how far absorption might be present in the capacity measurements. With iodine I was able to make some approximate measurements by a fall-of-potential method, which convinced me that the ordinary resistance of dry iodine is very high. As regards chlorine, I found that when prepared for experimental purposes the gas is always passed over a drying agent before liquefaction : an inspection of the capacity results, of which there are two or three separate determinations, led me to believe that the dielectric constants quoted are probably correct within a few per cent. This led me to bromine. I could, like Miss Anderson, at the time find no data as to its electrical resistance. I therefore procured the purest specimen I could and placed some in a U-tube with carbon electrodes. The resistance worked out at only 40 thousand ohms per cm. cube. On placing a few fragments of calcium chloride in the bromine the resistance soon increased to one megohm. As it was obvious there was still much moisture present, an attempt was made to distil the bromine, but without a well-organized chemical laboratory this was found both troublesome and dangerous. A friend then drew my attention to Professor H. B. Baker's work on highly-dried bromine, and I called on him and stated my difficulties and the object in view. He then kindly offered to place some of his highly-dried bromine at my disposal. The first specimen was in a rather narrow U-tube with platinum electrodes. I found it impossible to separate the resistance of this bromine from that of the glass tube in which it was contained. It was therefore clear that the resistance was far higher than the figures given above. The bromine remained in the tube for several weeks, and no action was observable on the platinum electrodes. This gave confidence to go further, and Professor Baker put up a further specimen of bromine in a glass bulb with platinum electrodes having about 5 cms.^{2} area each, spaced about a millimetre apart. Through the good offices of Mr. Dye, I was able to take this as soon as it was put up to the National Physical Laboratory ; here tests were made of the resistance, the figure found was 140 megohms. A subsequent test by myself some three weeks later, at a rather lower temperature, gave 160 megohms. These tests correspond with a specific resistance of about 10^{11} megohms per cubic centimeter, and accord satisfactorily with the figures found under better conditions by Miss Anderson. Tests were also made by Mr. Dye of the capacity over a range of frequencies from about 400 up to one million. The change of capacity with changing frequencies was only nominal over this great range. It was impossible to measure the dimensions and spacing of the electrodes, and the outside capacity, with a sufficient accuracy to obtain the dielectric constant of such a small specimen. I was, however, able to measure the dielectric losses over a range of frequencies from 4 per second to 1,250. The curve is similar to curves obtained with other liquid dielectrics of about the same resistance. Taking the loss at equal voltages in steady and alternating fields, and assuming the d.c. loss at unity, the losses in alternating fields were 192 at 17ω and 4·5 at $1{,}240\omega$. The results established clearly that Professor Baker's highly-dried bromine was a dielectric of a fairly high class, behaving in an ordinary manner for a liquid, and also that it could be kept in contact with platinum surfaces for some time without sufficient action to ionise it appreciably. In consultation with Professor Baker, the apparatus was then designed which Miss Anderson has used. It was still too small to enable good capacity measurements to be made by the method I was using ; but just at this time Dr. D. Owen drew my attention to the heterodyne method of measuring very small capacities, and mentioned that the Cass Institute was setting up the necessary apparatus. After inspection of the platinum condenser I already had made, he agreed that the method should be sufficiently sensitive to obtain the dielectric constant of bromine with it ; and on his telling me that Miss Anderson would be willing to undertake the work, it was placed at her disposal. That the work has been well done I am satisfied from my previous experience, and Miss Anderson is to be congratulated on the ability with which it has been carried out and for her patience and perseverance in dealing with a troublesome substance. Miss Anderson's work confirms within 2 or 3 per cent. the previous work of Schlundt and Schmidt, whose work I had previously relied on, but was inclined to doubt, because of the difference between their figures. The square of the refractive index for bromine is larger than that in the case of the other nine elements mentioned above, and it seemed to me that probably the larger relative

capacity was due to absorption. I think it is now fairly shown that this is not so. It was my intention with the above apparatus to have made more complete measurements of the losses in alternating fields over a wide range of frequencies than the approximate results given above, but I have been waiting to do this until Miss Anderson's work was completed. The ten elements I have mentioned above include all those occurring in organic matter; they also form a large number of compounds amongst themselves. Since matter itself, it is now agreed, is of electrical origin, it has for some years appeared to me of the first importance that the electrical properties of the non-metallic elements themselves in a pure state should be known as completely as possible. These elements form many compounds amongst themselves, of which many are dielectrics. Knowing the electrical properties of the constituents individually, we should then be in a position to study their properties when joined in compounds, and thus to trace differences brought about in their combination. There are other important questions turning upon the properties of this highly-dried bromine, but it would take too long to enter into them now; but I would like to end by paying a tribute to Professor H. B. Baker, whose beautiful work has enabled this further advance to be commenced on a solid foundation. There seem strong reasons for anticipating that these non-metallic elements are all in a pure and dry state high-class dielectrics and practically free from serious absorption. Absorption may, therefore, come in from combination or from the presence of some extraneous substance.

Dr. D. Owen said that, as regards the value found for the electric moment, it must be remembered that the bromine molecule is a heavy one, with some 40 electrons to the atom. The point raised by Mr. Hartshorn as to the effect of density variations on the temperature coefficient had been fully considered, and he thought the result must be taken as significant.

Author's reply: I quite agree that the bridge described by Mr. Hartshorn in his Paper to this Society is capable of a higher degree of accuracy than can be obtained by the method used in the present Paper owing to the inevitable break of circuit in the latter method, but it is unfortunate that bridge methods are inapplicable except at lower frequencies. The mercury cups were small and shallow, hence $\frac{1}{3}\mu\mu$F. would probably more nearly represent the value of the capacity across the disconnected switch than $1\mu\mu$F. I admit, however, the force of Mr. Hartshorn's criticism and that the effect of this error slightly reduces the accuracy originally claimed in the Paper for the value of the dielectric constant. Surprise was expressed by Prof. Richardson at the apparently large value deduced for the electric moment μ, but, on making the following calculation, I find that this value is considerably less than Prof. Richardson made it appear. Taking the electronic charge e as $4{\cdot}77\times10^{-10}$E.S., and, for the diameter of the bromine atom the value $2{\cdot}5\times10^{-8}$cm. used by Prof. W. L. Bragg and derived from X-ray grating measurements, we obtain the figure $11{\cdot}9\times10^{-18}$ for the product of electronic charge and diameter. This product is nearly 30 times the value $0{\cdot}40\times10^{-18}$ obtained for μ in the present Paper and is hence of a distinctly higher order than this value of μ. Similarly Gans and Isnardi's value of μ for liquid ethyl ether is given by Smyth (Phil. Mag. 47, p. 541, 1924) as $1{\cdot}435\times10^{-18}$. This is much higher than Mr. Hartshorn's estimate of $2\times0{\cdot}40\times10^{-18}$. I also feel that Mr. Hartshorn's line of criticism on the value found for μ, based apparently on chemical considerations, is one which must of necessity remain in abeyance until the present dearth of accurate data from actual observations by numerous observers has been removed. Since reading the present Paper before this Society, I have discovered that Dr. Smyth (Amer. Chem. Soc. J., 46, Oct., 1924) assigns the value $0{\cdot}58\times10^{-18}$ to the electric moment of the bromine molecule. I must, however, emphasize the fact that, since the final form of the dipole theory is hardly yet agreed upon, any value of μ here offered depends upon the application of experimental observations in the particular formula chosen and is therefore liable to revision. I fully agree with Mr. Black's observations. The term "polarization" used in the Paper was intended to include not only the back E.M.F. due to electrolytic action, but also the effect of a film of high resistance. This latter overwhelms the effect of the polarization E.M.F. when the current is reversed, and causes the rise shown in Fig. 3 of the Paper.

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